ANALYSIS OF ENEOLITHIC COPPER JEWELLERY ARTIFACTS FROM KSIĄŻNICE CEMETERY IN SOUTH POLAND

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Abstract

This paper presents a metallographic analysis of copper artifacts from an extraordinary Polish cemetery of Lublin–Volhynian culture dated 4000–3800 BC (Wilk in Analecta Archaeologica Ressoviensia, 2014, pp. 209–243). The Książnice necropolis, Busko-Zdrój county located in South Poland, is characterized by an unprecedented collection of prestigious objects made of copper, rare in the Eneolithic period in Poland. The archaeological studies supplemented with materials analyses give knowledge of prehistoric metallurgy and the processing of copper. For the described group of artifacts, non-destructive microscopic studies were performed including chemical analysis by means of X-ray fluorescence and energy-dispersive X-ray spectroscopy using a scanning electron microscope. The mentioned studies allowed for raw material characteristics of this important discovery.

Keywords: *archaeometallurgy, copper, Eneolithic, non-destructive testing, X-ray fluorescence, scanning electron microscopy-energy dispersive X-ray*

Introduction

In technology, a significant place is assigned to the history of metallurgy and foundry.[1] Archeological studies complemented by metallographic analyses reveal when prehistoric metallurgy and manufacturing methods of copper in the Eneolithic, and other periods was initiated in Central Europe.

Today distinct tracts of local smelting and casting of copper, fragments of clay molds or nozzles as well as copper items have been identified. Copper bars, wires and strips were produced from the smelted copper, which further was used in the production of decorative objects or, sometimes, tools. Rarely found objects were mostly imported from the Carpathian Basin, brought to the Polish lands by the people who had migrated after the Carpathians, supporting a thesis of possible trade exchange. Copper ornaments and tools from the late fifth and early fourth millennium BC represent a small group of prestigious character.

To the group of most important findings in Poland from that period belongs a metallurgical settlement in Złota near Sandomierz (South Poland, świętokrzyskie province) with well-preserved remains of molds, slags, ores and final products inserted into the graves nearby.[2] South of Lesser Poland province, the number of copper artifacts one can distinguish a cemetery of Wyciąże-Złotniki group in Krakow Nowa Huta-Wyciąże.[3,4]

The aim of this paper is the presentation of the material analysis of copper artifacts from the Polish cemetery of Lublin–Volhynian culture at site 2 in Książnice (Busko-Zdrój county, świętokrzyskie province), dated 4000–3800

BC. Site 2 in Książnice is located at the top of a hill (200, 15 m above sea level) at eastern part of Pińczów Hump (AZP 95-67: 100). Due to excavations (since 2001) led by Stanisław Wilk, it was possible to establish that the first settlement was located about 6000 years ago at this location. For the following 2000 years, it was used as a cemetery and settlement by various groups of the Eneolithic and Early Bronze Age populations.

Necropolis in Książnice is distinguished from other funeral habits of so-called Younger Danubian cultures in South-East Poland by incredible an accumulation of prestigious objects made of copper, rare during Eneolithic period in Poland. Among 17 graves, seven were equipped with copper ornaments and tools. Overall, 22 copper findings (bracelets made from copper wire and sheets, earrings made from wire, a necklace made from wire, spectacle shaped pendants, an earring, an axe, a hatchet, a chisel, an awl) came from this graveyard. This consists of the largest group of copper objects in Lesser Poland and one of the largest in all of Poland.[5]

Objects from this study come from grave no. 7 excavated in 2008. At the depth of 45 cm in a small rectangular burial pit oriented along NW–SE line, a skeleton of a child (most probably a girl), aged 9–10 years, was revealed.[6] The skeleton was lying in a flexed position on the left side with a skull pointing South (Figure 1).

One radiocarbon dating (Poz-27531) was performed on a material from grave no. 7 at Poznań Radiocarbon Laboratory. A date obtained from a fragment of a human rib was determined as 5180 ± 35 BP. After calibration, gives 4050–3940 BC at probability of 95.4 %.

A rich collection of artifacts was excavated in this grave: four clay vessels, one flake of Turonian flint and five copper objects.

Under the skull laid a massive wire earring (Figure 2a). Additionally, at the level of thorax, a cylindrical bead from a rolled sheet of copper was found (Figure 2c). Another such bead was found in a nearby water pipe excavation, which partly destroyed the tomb (Figure 2d), while the wire bracelet (Figure 2b), small ring and probably the other earrings (Figure 3e), were discovered approx. 30 cm to East of grave pit.

The analyzed burial belongs to a small group of rich Eneolithic infant/female graves found in Poland. Besides, in Lesser Poland, graves no. 2 and 8 from Książnice[7] and grave 390 from a site in Grodzisko I in Złota[8] are classified in this group. Particularly grave no. 8 contained as many as 10 copper objects demonstrates, as any other Eneolithic grave excavated in Poland, the extraordinary status of the buried women.[5]

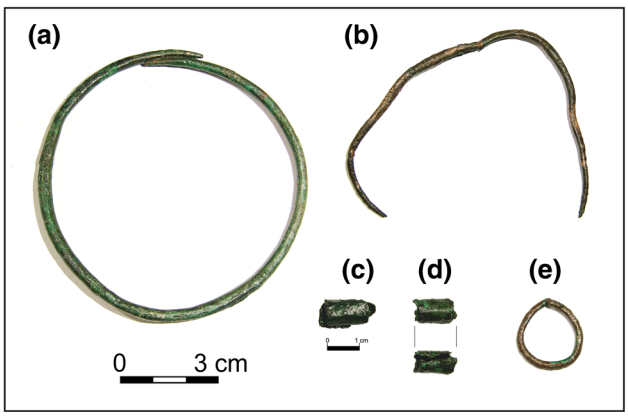


Figure 2. Copper jewellery from grave no. 7 of Lublin–Volhynian culture from site 2 in Książnice: (a) earring code no. Ks/w/18/08, (b) bent-out bracelet Ks/w/3/08, (c) cylindrical bead Ks/w/7/08, (d) cylindrical bead Ks/w/21/08, (e) earring Ks/w/4/08 (photograph by S. Wilk).

Figure 1. Grave no. 7 of Lublin–Volhynian culture from site 2 in Książnice during exploration, photograph S. Wilk.

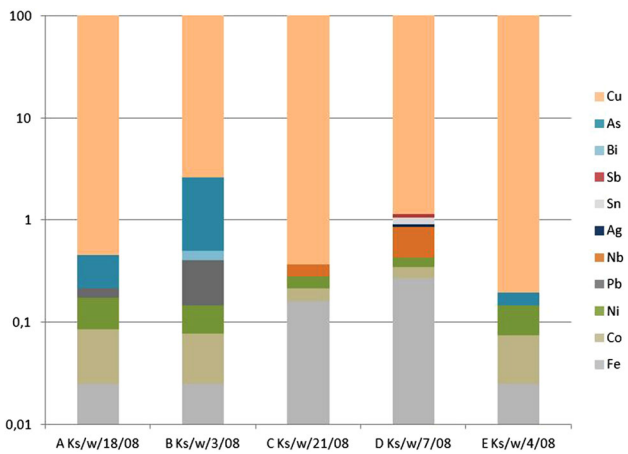


Figure 3. Chemical compositions log(wt%) of the artifacts from site 2 in Książnice.

Experimental Methods

Due to the historical value of the metal artifacts from Książnice, South Poland, it was not possible to prepare proper metallographic samples. For the given group of artifacts, only non-destructive tests directly on the objects were conducted. Surfaces for analyses were prepared by removing conservation coatings. Macroscopic and microscopic observations of the structures were performed. Additionally, chemical composition was determined by means of X-ray fluorescence spectroscopy (XRF) and energy-dispersive X-ray spectroscopy (EDS) using scanning electron microscopy (SEM).

The mentioned studies allowed for raw material characterization of this important discovery.[9]

Quite important was the observation of the prehistoric objects with respect to state of their preservation including identification of corrosion products. One should keep in mind that corrosion of copper archeological artifacts is an essential problem in conservation of metallic objects.[10–12]

Research

The materials analyses confirmed that the ornaments were indeed produced from copper. Very high concentration of copper is recorded in almost all of the artifacts: earring E (99.8 % Cu), bead D (99.6 % Cu) and earring A (99.5 % Cu) and bead C (98.8 % Cu). On the one hand, the smallest content of copper was in object B, a bracelet (97.5 % Cu). The discussed objects presented numerous impurities, important with respect to the origin of ore and smelting technology. The most important impurities include: arsenic, antimony, silver, tin, zinc, lead, bismuth, cobalt, nickel and iron. The highest impurity concentration occurred in bracelet B, where arsenic and lead exhibited significantly higher levels. The remaining findings presented a concentration of arsenic and lead. Zinc was identified in all analyzed items. Antimony and tin were present in bead C together with the highest content of silver, zinc, nickel, cobalt, iron and bismuth. Comparison of chemical composition results of the objects from Książnice is presented in Figures 3, 4, 5, and 6.

The selected artifacts (two earrings and a bracelet) were subjected to microscopic studies (Figures 4, 5, and 6).

Numerous fine defects in the form of irregular precipitates or their clusters were revealed in the background of uniform copper structure. The precipitates were localized mostly on the grain boundaries (Figures 4, 5, and 6). The identification was performed by means of X-ray fluorescence spectroscopy in microareas (Figures 7, and 8).

It was observed that in the vicinity of the regions comprised of pure copper (100 % Cu) that cavities were formed

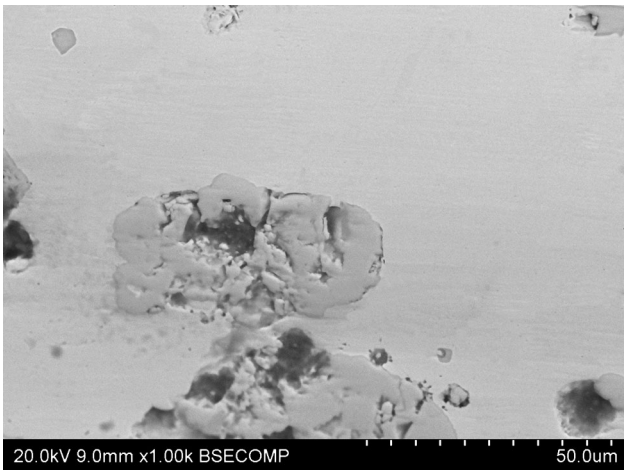


Figure 5. BSE micrograph of the bracelet B (Ks/w/3/08) microstructure.

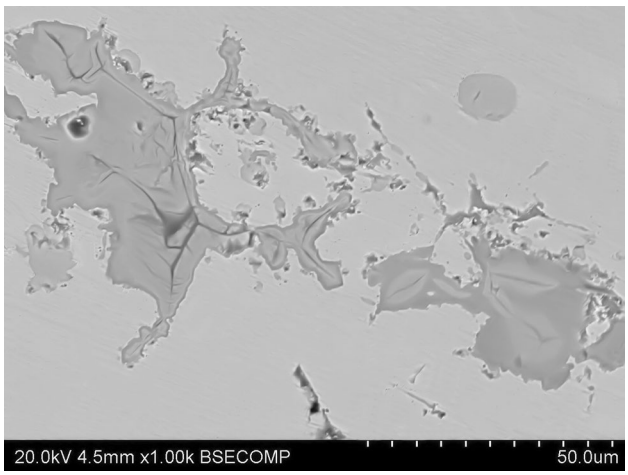


Figure 4. BSE micrograph of the earring A (Ks/w/18/08) microstructure.

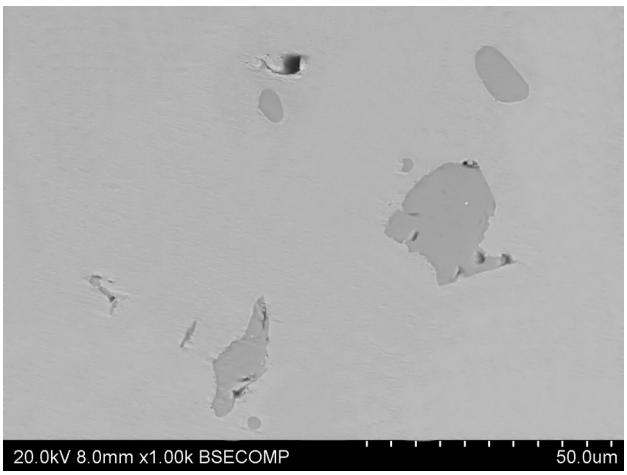
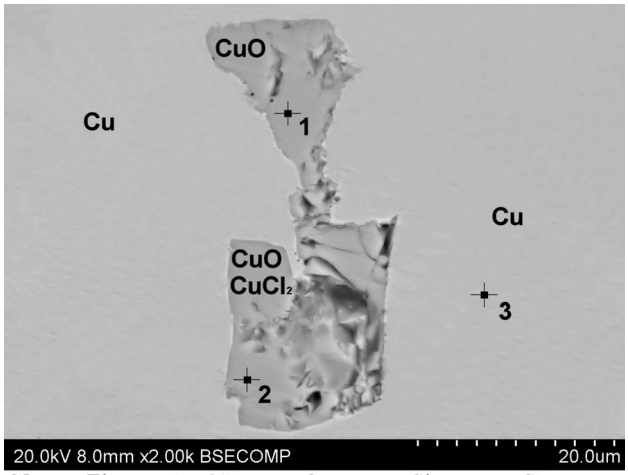
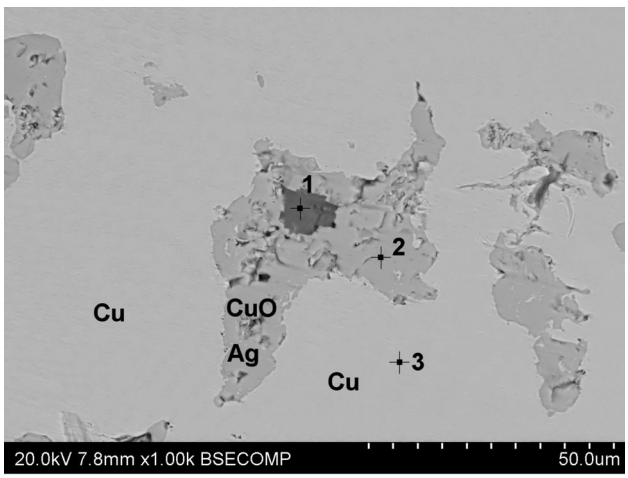


Figure 6. BSE micrograph of the circular earring E (Ks/w/4/08) microstructure.



No	Element (wt.%)	O	Cl	Cu
1.	**E** (Ks m 2) **pt 1**	18.08		81.92
2.	**E** (Ks m 2) **pt 2**	15.77	1.30	82.92
3.	**E** (Ks m 2) **pt 3**			100.00

Figure 7. Microstructure and chemical composition at marked areas (SEM–EDS) for the earring E; magnification 2000x.



No	Element (wt.%)	O	Cu	Ag
1.	**E** Ks/w/4/08 **pt 1**	43.40	56.60	
2.	**E** Ks/w/4/08 **pt 2**	18.56	72.22	9.22
3.	**E** Ks/w/4/08 **pt 3**		100.00	

Figure 8. Microstructure and chemical composition at marked areas (SEM–EDS) for the earring E; magnification 1000x.

filled with oxygen and chlorine compounds. The studies proved presence of copper corrosion products: copper oxides(II) (CuO) and copper chlorides(II) ($CuCl_2$) (Figure 7). Thus, structure in homogeneities is mostly caused by corrosion.

Some natural alloying additions were identified in the ores and artifacts. Silver, often found together with copper was identified in bracelet E in the form of silver precipitates (Figure 8). The rest of impurities were found in solid solution and along grain boundaries. The microhardness measurements of the chosen objects in the Vickers scale (HV) showed values 98–101 $\mu HV_{0,02}$, which is close to the value of pure copper, cold worked.[12]

Conclusions

Analyses of the Lublin–Volhynian artifacts from Książnice are included in archaeometallurgical studies on the oldest production methods of metals from Poland. The metallographic observations of the Eneolithic copper products allow for precise analysis of impurities in metal matrix.

Fire refining applied in Eneolithic and Bronze Age metallurgy did not provide entirely eliminate impurities; thus, the impurities can be regarded as an indicator of origin and technology. The differences in type and amount of impurities indicate origination from various geological deposits. The studied decorative objects were made mainly from copper with the most common impurities as: antimony, arsenic, bismuth, silver, cobalt, nickel, iron, zinc, lead and tin. The observed certain level of impurities and porosity indicated imperfection in technology. Thus, due to problems in removing trace elements, they were captured within the solid solution. With respect to the impurities concentration in the material, three of the studied artifacts had similar levels (99.5–99.8 % Cu), while one of them, bracelet denoted with letter B (Figure 3), was considerably different with respect to arsenic and lead. Most of the analyzed findings lacked antimony with the exception of bead C.

The jewellery from grave no. 7 of the Lublin–Volhynian culture at site 2 in Książnice was formed—most probably—by forging from liquid state. Considerably high content of copper (I) oxide (Cu_2O) in microregions and microscopic observations supports this thesis.

Widespread changes in the sample structure due to corrosive conditions from long-lasting deposition in the soil environment were observed. Pores within the bulk material proved presence of oxygen and chlorine. The corrosion products appeared to be connected with the presence of impurities in these regions, an effect of precipitation segregation to phase interfaces. The structure changes were visible at the grain boundaries that indicates intercrystalline corrosion. A result of corrosion activity of the material in the presence of oxygen is formation of copper oxide(I) (Cu_2O) and copper oxide(II) (CuO). Presence of chloride salts and a limited amount of oxygen caused formation of ($CuCl_2$). During microstructure observations, many fine regions that underwent corrosion were exposed. The ongoing corrosion process may weaken the structure, thus leading to cracking and material losses.

There are further studies planned for a group of 22 copper artifacts from the Książnice cemetery to determine manufacturing techniques of metal objects at the beginning of fourth millennium BC in Lesser Poland. Additionally, in comparison with similar collections excavated in different parts of Poland, it will be possible to determine a chemical characteristics and raw material relationships between groups. Studies on the current state and corrosion of artifacts are important for preservation of metallic objects.

Acknowledgments

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